SELF CRACK HEALING INDUCED BY HIGH TEMPERATURE OXIDATION IN SIN/SIC NANO-LAMINATED FILM

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ABSTRACT

In bulk, Si_3N_4 reinforced by dispersing SiC particle has superior self crack healing ability at high temperature. In consideration with this fact, SiN/SiC nano-laminated film is expected to exhibit the self crack healing at high temperature. In this study, we investigated the self crack healing behavior of the SiN/SiC nano-laminated film including its factors such as heating temperature, heating time.
The films were deposited on the silicon wafer using an ion beam assisted deposition technique. The SiN/SiC nano-laminated films with four layers were fabricated by alternative deposition of SiN and SiC. Total film thickness is approximately 1 μm. After the deposition, a pre-crack was introduced using a Vickers indentation. Then, the cracked film was heated using an electric furnace at temperatures ranging from 873 K to 1473 K in the air. The heating time was changed from 1 h to 72 h.
The crack on SiN monolayer film was almost not healed at the temperature less than 1273 K. On the other hand, in the case of SiN/SiC nano-laminated film, crack healing occurred at even 873 K. SiO_2 was observed along the healed crack. These results indicate that SiC layer contributes to crack healing significantly. However, the crack with large opening was not healed. These results indicate that SiN/SiC nano-laminated film has an ability to heal initial small crack.
The crack healing became remarkable with an increase in heating temperature and time. This result is corresponding with the tendency observed in bulk. However, at 1473 K, though the crack was healed perfectly, the laminate structure disappeared and the overall film was subjected to oxidation. This suggested that there is an upper limitation of temperature for in-situ self crack healing.

1. INTRODUCTION

Bulk silicon nitride (Si_3N_4) ceramics reinforced by silicon carbide (SiC) nanoparticles exhibits a self-crack-healing behavior at high temperature [1-2]. When a cracked ceramic is heated at high temperature in air, the SiC particles exposed on the crack plane thermochemically react to form silicon dioxide (SiO_2). As this reaction proceeds, the crack is filled by SiO_2 because the volume of SiO_2 is larger than that of SiC. Other research groups have reported that an Al_2O_3/TiC composite coating fabricated by plasma spraying also exhibits self crack healing by oxidation [3]. However, there are very few reports on self-healing micromaterials.

On the basis of the above reports, carbide composite thin films may also exhibit a self-crack-healing ability at high temperatures. The purpose of this study is to

fabricate SiN/SiC nano-laminated thin films with a self crack healing ability and investigate the influence of heating temperature and time on the self crack healing behavior.

2. EXPERIMENTAL PROCEDURES

The SiN/SiC nano-laminated films were deposited on Si(100) substrates by an ion beam assisted deposition [4]. The substrates were cleaned by successive rinsing in ultrasonic baths of acetone. After cleaning, the Si substrates were fixed on a water-cooled holder. After setting the substrates, the chamber was evacuated to a base pressure of 1×10^{-3} Pa.

The SiN/SiC nano-laminated films were fabricated with alternating layers of SiN and SiC. The deposition conditions for the layers are shown in Table 1. The SiN layer was obtained by electron-beam evaporation of pure silicon and simultaneous bombardment by a nitrogen-ion beam. The SiC layer was deposited by the electron-beam evaporation of silicon and simultaneous bombardment by an argon-ion beam under an ethylene atmosphere [5]. The fabricated nano-laminated film consisted of four layers with the top layer being SiN. The bilayer thickness was fixed to 500 nm and the bilayer ratio of SiN to SiC was 1. The SiN monolayer films were also fabricated to compare their properties with that of the SiN/SiC nano-laminated film. The total thickness of all the films was 0.9–1.2 μm.

A small artificial crack was introduced using a Vickers micro-indenter. The crack length was 10–15 μm. The cracked films were heated using an electric furnace in an air atmosphere. In this study, the self-crack-healing behavior of the nano-laminated films was systematically investigated by changing the heating temperature (873–1473 K) and time (24–96 h). The films were observed by field emission type scanning electron microscope (FE-SEM) every 24 h.

3. RESULTS AND DISCUSSION

Figure 1 shows the FE-SEM images of the crack after heating the samples at a temperature of 1073 K for 24 h. In the case of the SiN monolayer film, the crack was poorly healed after heating, as shown in Figure 1(a), respectively. On the other hand, the cracks in the SiN/SiC nanolaminated films were healed, as shown in Figure 1(b). In bulk, when Si_3N_4 and SiC are heated in air, oxidation occurs by the following chemical reactions:

Table 1: Deposition conditions.

	SiN	SiC
Arc voltage (V)	80	
Ion beam	Nitrogen	Argon
Gas flow rate (sccm)	4.0	1.5
Acceleration voltage (keV)	2.0	0.3
Acceleration current (mA)	14.0	15.0
Atmosphere gas	-	Acetylene
Vapor rate (nm/s)	0.2	0.1

$$SiC + 3/2\,O_2 \rightarrow SiO_2 + CO \quad (1)$$

$$Si_3N_4 + 3O_2 \rightarrow 3SiO_2 + 2N_2 \quad (2)$$

The theoretical volume expansions caused by these reactions are calculated to be approximately 80% and 69%, respectively. These volume expansions results in crack healing. However, the crack healing in the SiN films did not almost occur, while it was observed in SiN/SiC nanolaminated films. This suggests that the activation energy of oxidation in SiC is lower than that in SiN [6]. Therefore, it can be concluded that the SiC layer is the major contributing factor to crack healing in the SiN/SiC nanolaminated films.

The influence of the heating temperature on the self-crack-healing behavior was investigated. The heating temperature was varied from 873 to 1473 K and the heating time was fixed at 24 h. Figure 2 shows the FE-SEM images of crack after heating. Slight crack healing occurred at 873 K. Crack healing improved with an increase in the heating temperature, and heating at 1273 K perfectly healed the crack. However, at 1473 K, the laminated structure disappeared because of oxidation even though the crack was healed. This suggests that the SiN/SiC nanolaminated cannot use cyclically for sefl-heaking material once the film is heated at temperature over 1473 K.

The influence of heating time on the self crack healing behavior was also investigated. The heating time was varied from 24 to 96 h at temperatures of 873 K.

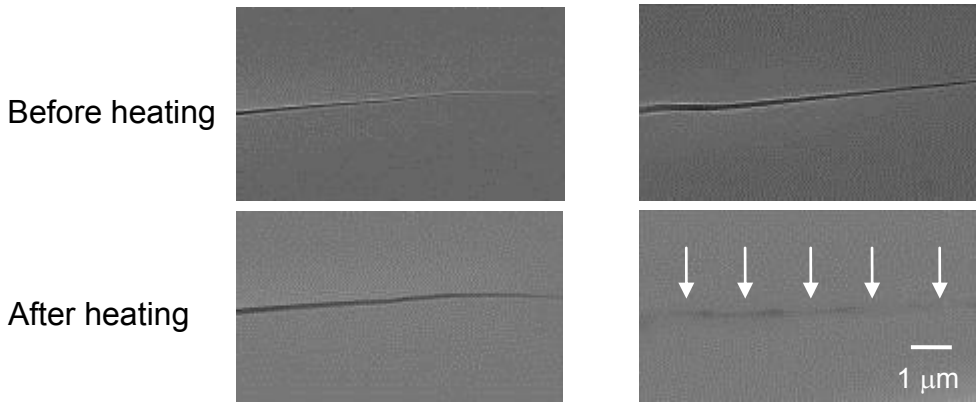


Figure: 1 FE-SEM images of crack tip before and after heating. The upper and below images indicate crack before and after heating respectively.

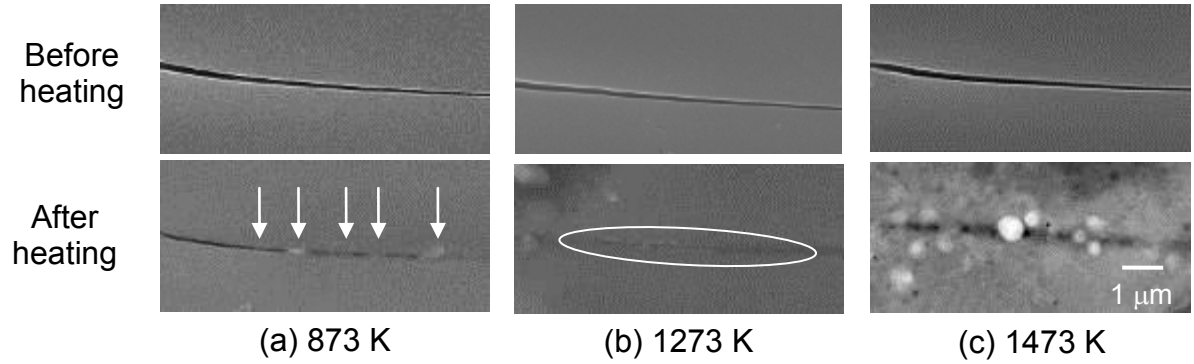
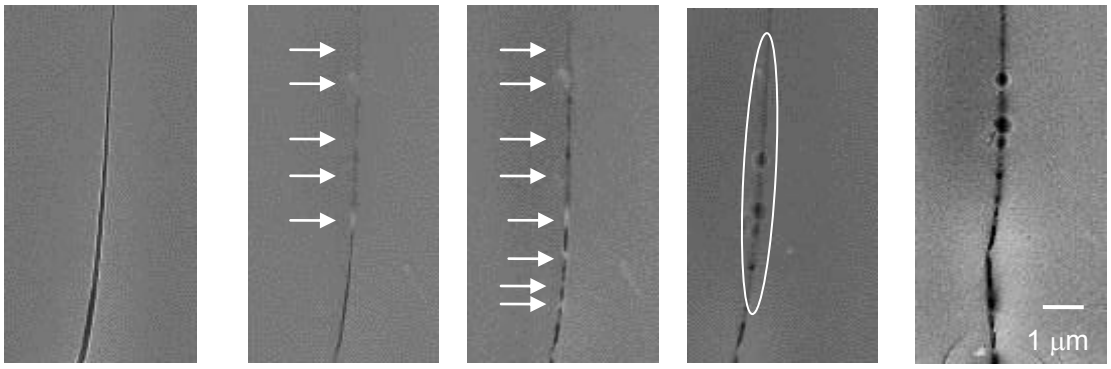


Figure 2: Influence on heating temperature on the crack healing. The upper and below images indicate crack before and after heating respectively.



(a) Before heating (b) After 24h (c) After 48h (d) After 72h (e) After 96h

Figure 3: Influence on heating time on the crack healing in SiN/SiC film.

Figure 3 shows the FE-SEM images of the cracks after heating. The crack healing improved with an increase in the heating time. However, the crack healing stopped after heating for 72 h despite the crack did not heal perfectly.

4. CONCLUSION

In this study, the self-crack-healing ability of SiN/SiC nano-laminated thin film under high temperature environment was investigated. In SiN monolayer film, cracks were poorly healed because the size of the crack opening increased significantly during heating. On the other hand, SiN/SiC nano-laminated films exhibited a superior self-crack-healing ability. Crack healing was promoted by an increase in the heating temperature and time. However, at temperatures over 1473 K, the laminated structure disappeared and the film was subjected to oxidation overall.

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